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Fiber Optic Raman Spectroscopy for Detection of Methane Hydrates and Related Species

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13. ABSTRACT (*Maximum 200 words*)

A capillary waveguide fiber optic probe system has been constructed which is capable of rapidly collecting Raman spectra of organic compounds in water. It consists of a dual fiber optic probe coupled to a capillary waveguide designed to increase the volume of sample interrogated by the excitation light. A Nd:YAG laser operating at 532 nm is used to generate Raman scatter at the sample in the capillary which is transmitted by the collection fiber to a notch filter holder and linear array detector. The feasibility of using this system for methane hydrate detection is evaluated through the use of organic surrogate molecules, due to the low solubility of methane in water at atmospheric pressures. The eventual application is the oceanic detection of methane gas, liquid, and solid hydrate at great depths (1000's of meters). Under these conditions, the solubility of methane increases significantly and solid hydrate may be present. The relative Raman cross sections of methane and other organic compounds relative to nitrogen are documented. The benefit of using a capillary waveguide with the dual fiber optic probe is quantitatively shown. The LOD of acetone (as a surrogate for methane) is determined and the LOD of methane under several experimental conditions is calculated. The ability to detect all three states (gas, liquid, and solid) is of great importance to the detection and characterization of ocean floor methane.

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FIBER OPTIC RAMAN SPECTROSCOPY FOR DETECTION OF METHANE HYDRATES AND RELATED SPECIES

INTRODUCTION

The detection of methane hydrates in the deep ocean environment is essential for the characterization of potential natural gas resources. Current technologies being deployed suffer from limitations including non-specificity, complexity, and slow response times. Optical methods afford the most flexibility with respect to methane hydrate detection. There are three regimes in which methane detection is desired: as a solid, as a gas in water, and dissolved in water. Optical spectroscopy allows measurements to be made in all three scenarios. In particular, Raman spectroscopy provides a wealth of analytical information regarding not only methane but many related hydrocarbons (ethane, propane, etc.) and potentially other species that contaminate the hydrates. Knowledge of the type and quality of hydrate present at a given location would be invaluable for the assessment of various locations of hydrated natural gas.

Initial studies to determine the feasibility of using Raman spectroscopy for the analysis of methane hydrates indicate that Raman probes may be useful in the characterization of oceanic environments including gaseous, liquid methane in sea water and methane hydrate. Raman spectroscopy is a well-established technique and is an attractive approach for deep oceanic environments due to its remote operability either through a window or when coupled to fiber optics.[1,2] The use of optical fibers is ideal for ocean deployment for two reasons: 1) Measurements can be directed towards an area of interest using a robotic arm, and 2) damage can be restricted to the fiber optic probe not the laser and spectrometer. Due to the inherently weak nature of Raman scattering, a capillary waveguide approach is taken to increase the collected Raman scatter of the sample.

We are proposing to use the second harmonic (532 nm, 18,797 cm^{-1}) of a Nd:YAG laser for Raman excitation of methane C-H vibrational bands. The detection of other small hydrocarbons (ethane, propane, etc.) that often indicate the presence of a methane source will be investigated through excitation of C-C and -CH_3 vibrational modes. The use of a miniature spectrometer will be investigated and tested with respect to sensitivity and resolution. Initially, liquid organic materials have been studied neat and diluted in water as a simple substitute for methane, whose solubility is very low at atmospheric pressure, rendering the concentration too low to be measured with the available detector. A list of the normalized Raman cross sections (N_σ) is given in Table 1 for comparison.[3,4] The Raman cross section is a measure of the efficiency of inelastic photon scattering versus the elastic Rayleigh photon scattering which produces no change in frequency. For example, when compared with nitrogen, methane has a Raman cross section which is 9.0 times greater, acetone has a cross section which is 2.4 times greater, and water's Raman cross section is 3.4 times greater. Due to its lower relative Raman cross section and methyl groups, and high solubility in water acetone was chosen initially as a substitute for methane.

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Table 1. Relative Normalized Differential Raman Scattering Cross Sections (N_σ) for Vibrational Bands of Various Molecules

Molecule	ν_j (cm^{-1})	Exciting λ (nm)	Normalized σ	Ratio $N\sigma(X) / N\sigma(CH_4)$
N_2	2331	515	1.0	0.1
H_2	4156	515	3.4	0.4
CH_4	2917	515	9.8	1.0
C_2H_6	993	488	1.2	0.1
C_3H_8	2890	515	6.6	0.7
	867	515	1.7	0.2
H_2O	3652	515	3.4	0.4
CH_3OH	2955	515	10.9	1.2
	2846	515	6.9	0.8
C_2H_5OH	2943	515	25.6	2.8
$CHCl_3$	773	515	1.6	0.2
CCl_4	459	515	6.95	0.8
C_6H_6	3070	515	15.3	1.7
	992	515	12.1	1.3
C_6H_{12}	802	515	4.1	0.5
$(CH_3)_2CO$	782	488	2.4	0.3

EXPERIMENTAL

The system used for feasibility testing consisted of a Nd:Yag Laser operating at 532 nm (18,797 cm-1) with a power of 35 mW at a repetition rate of 15 Hz and a pulse width of 3-5 ns. Light was injected into a 600 μm excitation fiber (FVP600630660, Polymicro Technologies, Phoenix, AZ) using a 200 mm focal length lens (Model No. 41380, Oriel, Stamford, CT). The fiber was held in place using a fiber chuck (Newport, CA) mate to a X-Y positioner (New Focus, CA) to align the fiber face with the excitation beam. All incident excitation energies were measured at the distal end of the excitation fiber using a detector head (LM-1, Coherent, Auburn, CA) and a digital meter (Fieldmaster GS, Coherent, Auburn, CA). The 600 μm excitation fiber was one of two fibers in dual parallel fiber design probe, one delivering light and the other 600 μm collection fiber gathering the Raman scatter. The collection fiber was terminated using a SMA-905 fiber optic connector interfaced with a fiber optic breakout filter holder containing a holographic 532 nm notch filter. A 400 μm fiber on the opposite end of the filter holder delivered the Rayleigh line-filtered Raman scatter to an miniature spectrometer (PC2000, Ocean Optics, Dunedin, FL), an uncooled linear CCD array, via another SMA-905 fiber optic connector using an integration time of 5 sec. Spectrometer slits were not present, thus the input optical fiber (400 μm) defined the effective slit resulting in a resolution of approximately 150 cm^{-1} (FWHM). While this represents low

resolution Raman spectroscopy, identification of organic species is readily possible as will be demonstrated in the following section. A diagram of the optical layout of the system is given in Figure 1. All measurements were made using the capillary waveguide, which consisted of a 2 mm i.d., 2.4 mm o.d. fused silica tube (Vitrocom Inc, Mt. Lakes, NJ). The ends of the dual fiber optic probe were inserted into the end of the capillary waveguide as depicted in Figure 2.

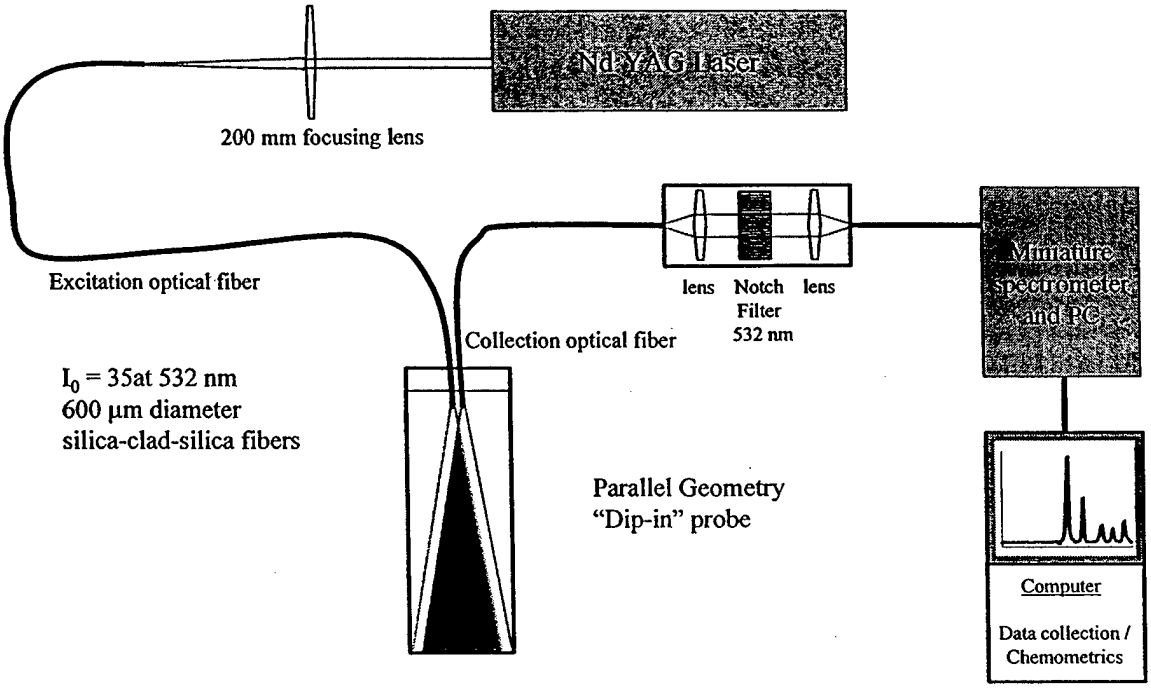

Figure 1. Nd:YAG laser using the 2nd harmonic output coupled to a fiber optic probe with a fiber breakout and notch filter for Raman spectroscopy

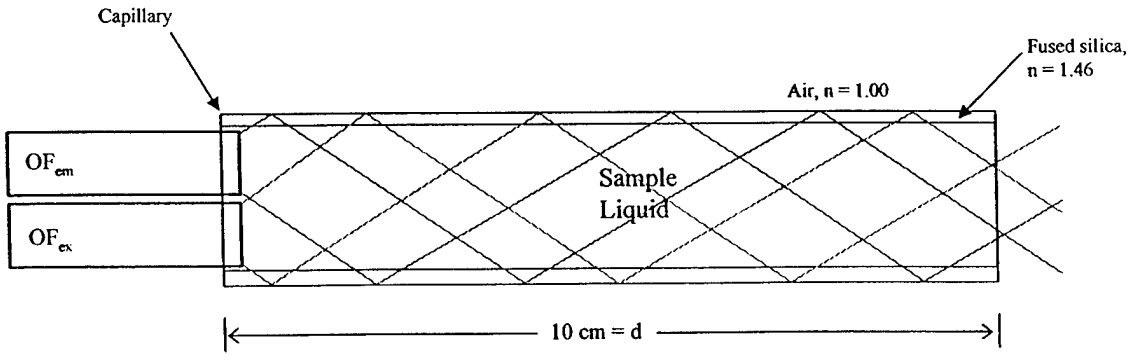

Figure 2. Capillary waveguide showing the rays of light emanating from the excitation fiber (OF_{ex}) and collection or emission fiber (OF_{em})

RESULTS

The use of a capillary waveguide / dual fiber probe combination in air with the sample solution inside the capillary enables a significant increase in signal to be realized at very little cost to the end user. This can be seen in Figure 3, where spectra of a neat solution of acetonitrile have been taken using a two fiber parallel "dip-in" probe with and without a capillary waveguide attached. The effect of the capillary is a four-fold increase in signal: for the 2935 cm^{-1} band of acetonitrile, the two fiber probe signal level was 525 counts versus the signal obtained using the capillary waveguide, 2050 counts.

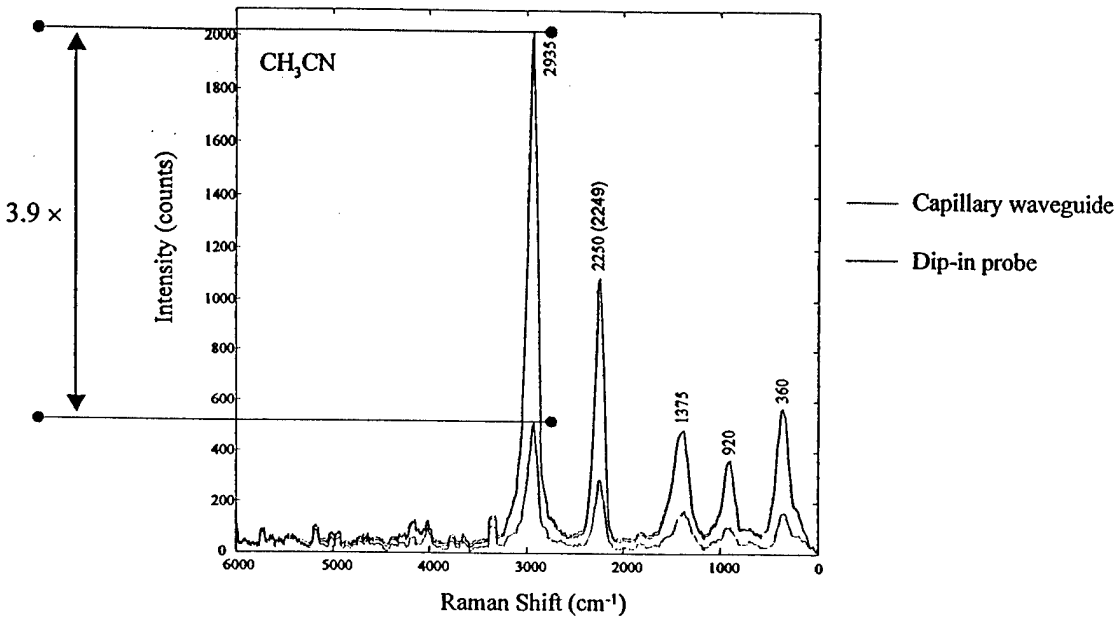

Figure 3. Capillary waveguide enhancement of Raman signal of an acetonitrile (CH_3CN) solution

The ability to measure low resolution Raman spectra using an inexpensive uncooled linear CCD can be seen in Figures 4 and 5. Many bands are visible in the Raman spectrum of neat toluene in Figure 4, as are visible in the spectrum of neat chloroform ($CHCl_3$) in Figure 5. The Raman spectrum of a mixture of hexane isomers is shown in Figure 6. Five bands in the spectrum of hexane are easily identifiable, even at this reduced resolution. The separately measured overlaid Raman spectra of water and acetone, in Figure 7, shows that they should easily be identifiable in a mixture.

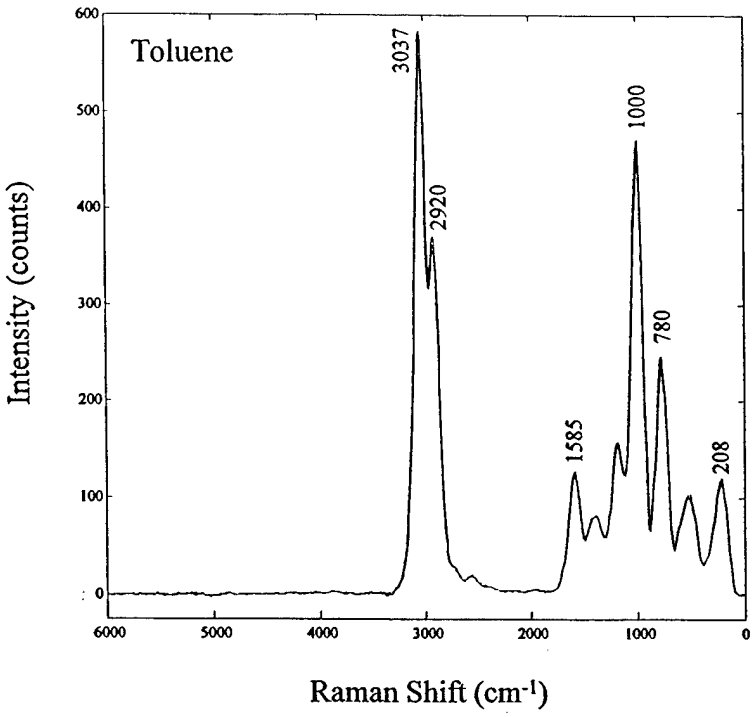

Figure 4. Raman spectrum of neat toluene using the capillary waveguide fiber optic system. Three spectra are measured in series are overlaid in the plot

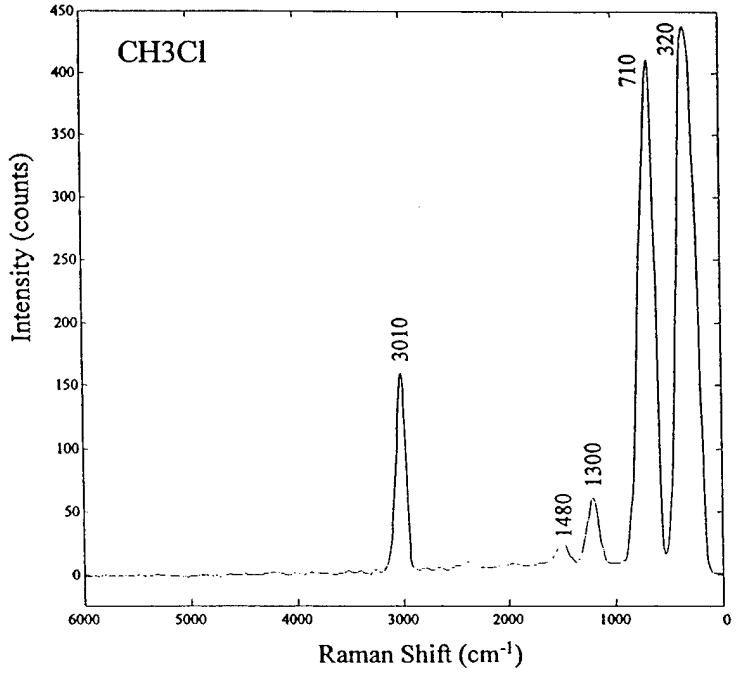

Figure 5. Raman spectrum of neat chloroform ($CHCl_3$) using the capillary waveguide fiber optic system

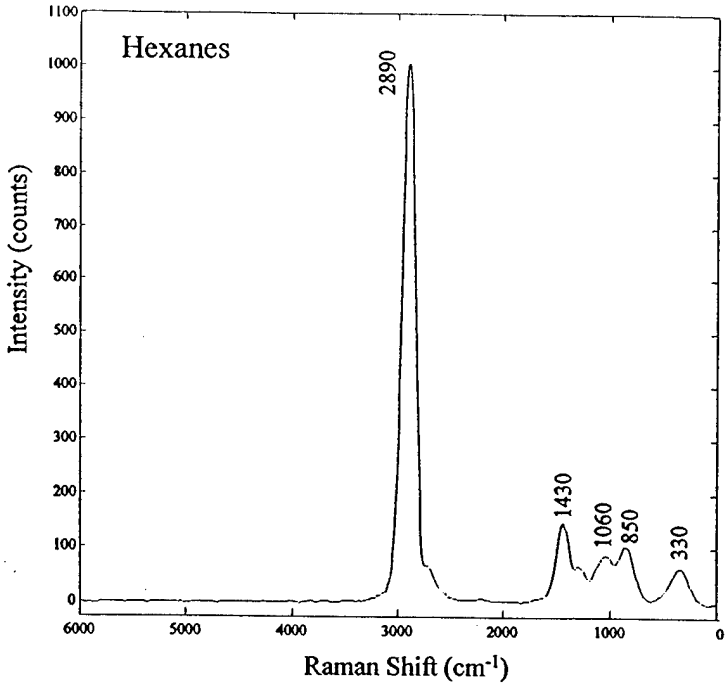

Figure 6. Raman spectrum of a mixture of neat hexane isomers using the capillary waveguide fiber optic system

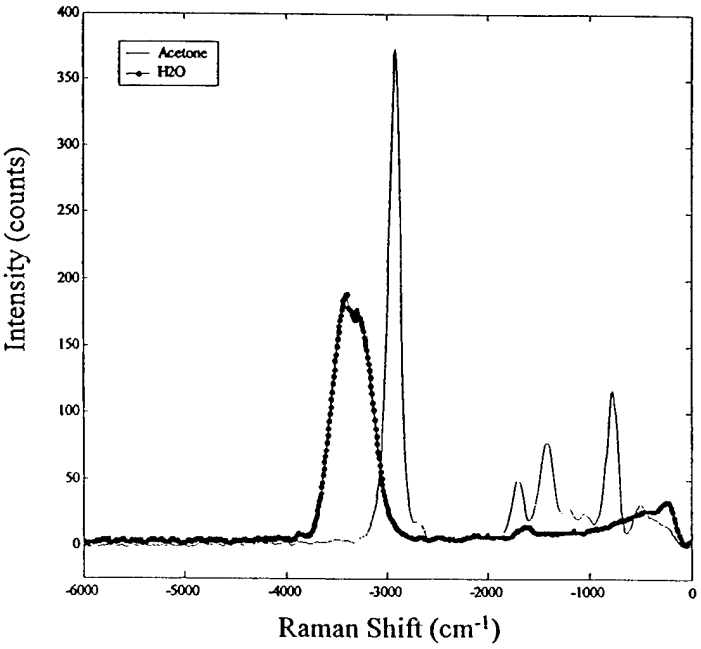

Figure 7. Overlaid Raman spectra of water (dots) and acetone (line) using the capillary waveguide fiber optic system

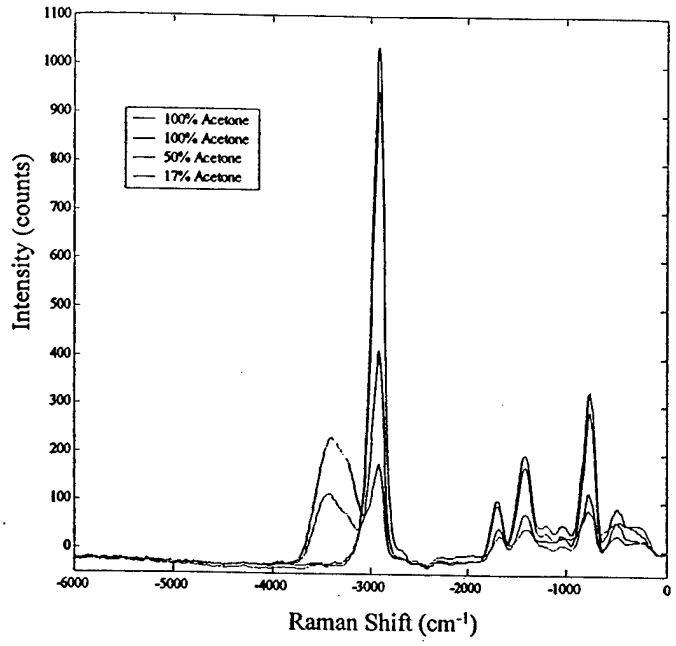

Figure 8. Raman spectra of acetone and water mixtures measured using the capillary waveguide fiber optic system

The spectra of several concentrations of acetone in water are given in Figure 8. Using acetone in water as a surrogate a calibration curve was generated and the resulting acetone calibration curve is shown in Figure 9. Accounting for the difference in the Raman cross-sections, the estimated limits of detection (LOD) and limits of quantitation (LOQ) for methane were calculated assuming higher laser powers and integration times. The use of a new detector which has better charge coupled device (CCD) sensitivity and a light collection lens provides a factor of 50 in terms of sensitivity according to manufacturers specifications. This improvement combined with integration time and laser power increases will permit the detection of methane in this application. These calculated LOD are consistent with the concentrations of methane expected at depth and are summarized in Table 2.

Table 2. Experimental Modifications and LOD Improvement of Acetone and Methane

Experimental modification	Improvement Factor	LOD (%)	LOQ (%)
Acetone with current detector, 35mW, 5 s integration tin	-	2.1	6.9
Acetone with new detector, 35mW, 5 s integration time	50	4.2×10^{-2}	1.4×10^{-1}
Acetone with new detector, 100mW, 5 s integration time	145	1.4×10^{-2}	4.7×10^{-1}
Acetone with new detector, 100mW, 10 s integration tim	290	7.2×10^{-3}	2.3×10^{-2}
Methane with new detector, 100mW, 5 s integration time		3.6×10^{-3}	1.2×10^{-1}
Methane with new detector, 100mW, 10 s integration time		1.9×10^{-3}	6.2×10^{-2}

* LOD - limit of detection; LOD is baseline + 3s

* LOQ - Limit of quantitation; LOQ is baseline + 10s

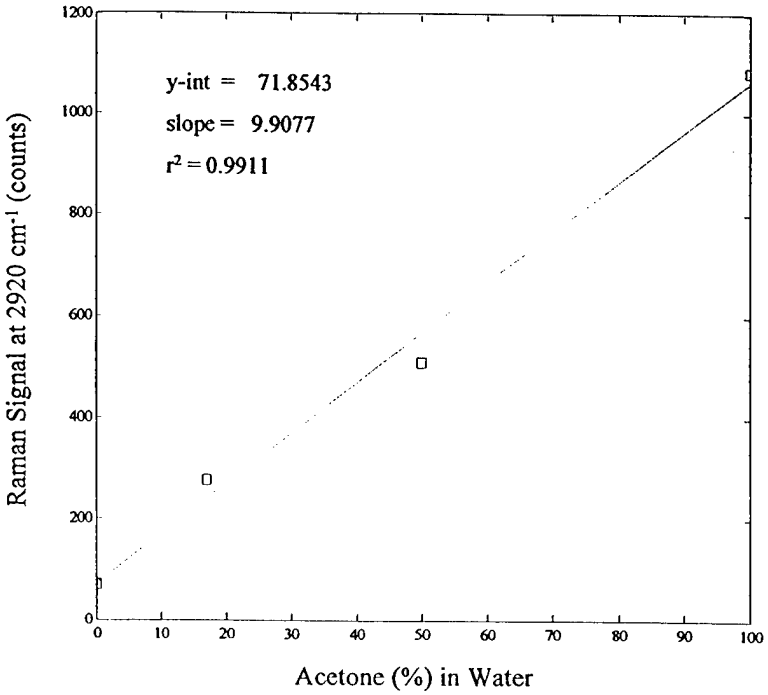

Figure 9. Analytical calibration curve for acetone in water

CONCLUSIONS

The use of a capillary waveguide provides a significant increase in the measured Raman signal from organic molecules. This optical configuration combined with several improvements/modifications in the analysis method and instrumentation, will permit the measurement of methane and related molecules at depth.

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